

11/PRTS

1 SECURITY PRINTING

2

3 The invention relates to materials and techniques  
4 relating to security printing.

5

6 The present invention in its broadest sense is  
7 concerned with the provision of security in relation to  
8 documents, vouchers, packaged goods and tokens of  
9 value. Examples of these are banknotes, cheques and  
10 drafts, bond and stock certificates, and credit and  
11 bank cards. All of these are referred to hereinafter  
12 for simplicity as "documents".

13

14 Documents of this nature have the requirement to be as  
15 secure as possible against forgery and falsification  
16 and for this purpose it is desirable that they exhibit  
17 both covert and overt security features. The  
18 expression "covert security feature" is used to denote  
19 some security feature which is not visually apparent to  
20 the normal user, whereas "overt security feature" is  
21 used to denote a feature which can be readily seen and  
22 recognised by members of the public without the use of

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1 specialised equipment or confidential information.  
2 Traditional forms of overt security features include  
3 water marks, metal security threads, and the use of  
4 specialised forms of paper and printing.  
5

6 Known methods of covert security include NIR and IR  
7 absorber inks, magnetic threads, complex optical and  
8 electrically conductive indicia, anti-Stokes, visible-  
9 wavelength-emitting phosphors etc.  
10

11 With rapid advances in reprographic technology such as  
12 relatively cheap and high quality colour photocopiers  
13 and easily available digital image manipulation, the  
14 traditional forms of security have become increasingly  
15 easy to circumvent. This is because the absorption and  
16 emission in the visible, NIR and IR ranges of all the  
17 currently used and proposed security dopants are  
18 readily available in the public domain since the  
19 current materials were developed for the laser and lamp  
20 industries. This is particularly true for all the rare  
21 earth containing absorbers and emitters, where many  
22 thousands of public domain references of absorption and  
23 emission spectra are listed from the 1950's onwards.  
24 There is accordingly a requirement for improved forms  
25 of both covert and overt security features, preferably  
26 ones which can be used with existing printing  
27 technology at modest cost.  
28

29 According to one aspect of the present invention, there  
30 is provided a method of providing a document with a  
31 covert security feature, in which the document is

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1 printed using an ink containing a dopant, the dopant  
2 being of a material which can be identified by  
3 examination of its response to visible wavelength  
4 photon radiation.  
5

6 This and other aspects and features of the present  
7 invention are defined in the appended claims.  
8

9 The present invention will now be described by way of  
10 example with reference to the accompanying drawings of  
11 which:  
12

13 Fig. 1 shows a blue ink reflectance spectrum from a  
14 paper print;  
15

16 Fig.2 shows green ink reflectance spectrum from a paper  
17 print;  
18

19 Fig.3 shows red ink reflectance spectrum from a paper  
20 print;  
21

22 Fig.4 shows a reflectance spectrum from the  
23 Praesodymium Oxide dopant in accordance with the  
24 present invention;  
25

26 Fig.5 shows a reflectance spectrum from the Neodymium  
27 Oxide dopant in accordance with the present invention;  
28

29 Fig.6 shows a reflectance spectrum from the Holmium  
30 Oxide dopant in accordance with the present invention;

1

2 Fig.7 shows a reflectance spectrum from the Thulium  
3 Oxide dopant in accordance with the present invention;

4

5 Fig.8 shows a reflectance spectrum of raw Europium  
6 Oxide powder as used in the present invention;

7

8 Fig.9 shows a reflectance spectrum of the same  
9 Europium Oxide contained in glass;

10

11 Fig.10 shows a reflectance spectrum of raw Erbium Oxide  
12 powder as used in the present invention;

13

14 Fig.11 shows a reflectance spectrum of the same Erbium  
15 Oxide contained in glass;

16

17 The present invention provides a range of inorganic  
18 dopants designed with absorption spectra sufficiently  
19 different in form and structure from the absorption  
20 spectra of printing inks so that the dopants can be  
21 easily identified. They thus become very covert because  
22 they exhibit no UV, visible or IR stimulated output to  
23 be observed by a counterfeiter.

24

25 The preferred elements for our dopants can be fused  
26 with other elements in order to hide the presence of  
27 the dopant element, or to alter its absorption  
28 spectrum; or the oxide or salt of preferred element  
29 itself can be directly mixed into, for example, a  
30 printing ink or a batch composition for plastics  
31 production etc. When the dopant is mixed with other

1 elemental compounds and where one of its admixture  
2 compounds contains a substantial proportion by weight  
3 of a particular range of atomic number (z) elements,  
4 varying the proportion of this compound in the final  
5 mix can vary the absorption spectrum of the final  
6 inorganic mixture, thus essentially creating further  
7 dopants.

8  
9 The present invention depends on the incorporation of a  
10 synthesised inorganic dopant into or onto the document  
11 at any stage of its manufacture, including the printing  
12 stage. These dopants are designed to have very complex  
13 visible wavelength absorption spectra, measured in  
14 either reflective or transmissive mode. The spectra  
15 they exhibit are not found in printing inks or common  
16 marbling substrates. This results in high signal-to-  
17 noise ratio detection, and hence the ability to  
18 identify the dopant in 10msec or less using low output  
19 (c. 4W) bulbs as illuminants.

20  
21 The dopant incorporation with its unique spectrographic  
22 pattern gives independence from document soiling, wear  
23 and tear etc, because it allows excellent signal-to-  
24 noise ratio. Pattern recognition software to identify,  
25 within 1 msec, the complex signature of our synthesised  
26 dopants is readily available from suppliers in the  
27 public domain, having been used in optical and nuclear  
28 spectrometry for 30 years. Dopants in accordance with  
29 the present invention can be incorporated singly,  
30 mixed, or in separate areas to produce a "bar code", or  
31 to simply confuse a forger. The dopants, depending on

1 composition, are either colourless or transparent, or  
2 coloured, at the choice of the user. Dopants made in  
3 accordance with the present invention provide high  
4 optical absorption yet give optical transparency  
5 because their absorption features are created at  
6 wavelengths to which the human eye is insensitive.

7  
8 For visible wavelength interpretation the preferred  
9 method is to illuminate an area of at least 5mm<sup>2</sup> by a  
10 ring of at least 6-8 200µ optical fibres in a  
11 concentric ring, and channel reflected light through an  
12 inner 200µ optical fibre to the wavelength detector. It  
13 has been found that this number of optical fibres gives  
14 sufficient signal for interpretation of the spectra,  
15 however the present invention is not limited to this  
16 method of detection of the spectrum or the number or  
17 arrangement of optical fibres used in this detection  
18 method. This eliminates the optical losses due to  
19 lenses in much prior art, which in turn leads to the  
20 processing speed of our system. CCD based wavelength  
21 detectors, followed by A-D conversion for processing  
22 are standard technologies in public domain electronics.  
23 Our dopants are engineered to give no visible signal,  
24 such as fluorescence, upon illumination by UV, visible,  
25 or IR radiation and are hence not easily replicated as  
26 has happened with fluorescent inks, and other emitting  
27 technologies.

28  
29 The advantages of the present invention will be readily  
30 apparent when the spectra obtained from these dopants

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1 is compared with those obtained from standard printing  
2 inks, or colourisers in plastics etc. The standard  
3 inks and the like give relatively unsophisticated  
4 reflectance spectra - see for example Figures 1, 2, 3.  
5 These show the visible reflectance spectrum of a  
6 Pantone standard blue, green and red ink from a paper  
7 print. Figures 4, 5, 6, 7 show the visible reflectance  
8 spectra from the four dopants, Praesodymium Oxide, the  
9 Neodymium Oxide, the Holmium Oxide and Thulium Oxide,  
10 incorporated in a clear litho varnish and printed on  
11 the same paper as that used to obtain the spectra shown  
12 in Figs. 1, 2 and 3.

13  
14 The prints obtained using dopants in accordance with  
15 the present invention are completely colourless to the  
16 eye. Figure 4 for example, shows many easily  
17 identifiable peaks, troughs and turning points in its  
18 spectrum with a shape easily distinguished from any ink  
19 or colouring dopants. It is these unique features  
20 which give the excellent signal-to-noise ratio, giving  
21 the rapid identification ability of our system, with  
22 excellent identification rates, and very low false  
23 acceptances, together with high rejection for forged  
24 copies.

25  
26 The features, and/or slopes, of the reflectance spectra  
27 can be shifted to create other dopants by incorporating  
28 the dopants into inorganic compounds of the type  
29 described later.

30

1 The use of visible wavelength spectrometry, as opposed  
2 to IR or NIR wavelengths, makes possible many more  
3 commercial applications. This is firstly because of  
4 the reduced cost of components for the visible, and  
5 secondly because the cheapest excitation source is a  
6 common (4W) torch bulb which emits plenty of visible  
7 light but very little IR. Hence IR and NIR techniques  
8 require more powerful and costly excitation sources.  
9 Also by moving to the visible we make it easy to  
10 construct simple hand-held portable instrumentation  
11 which again increases possible commercial applications.

12  
13 Visible wavelength spectroscopy as revealed in the  
14 prior art with application to security uses lenses or  
15 mirrors and lamps to provide the illumination source.

16  
17 Many suppliers, such as Oriel Corp. USA, now make  
18 commercially available reflectance probes which are  
19 about 6mm diameter overall and contain a ring of  
20 illuminating fibres (200µ diameter 6-8 in number)  
21 surrounding a centre core of detecting fibres. Use of  
22 these probes gives much improved signal-to-noise ratio  
23 at the CCD array, or Si photodiode array, or other  
24 detector. Using other off-the-shelf components the  
25 output of the array spectrometer can be coupled to D-A  
26 converters and operated from a laptop, hand-held  
27 palmtop, or desktop PC computers. This can easily be  
28 interfaced to standard computer software on production  
29 lines for authentication at high speed - 10m/sec.



1 The dopants we have identified as working well can be  
2 added to standard offset litho printing inks in a  
3 manner known to those skilled in the art. It is added  
4 in quantities up to about 30% by volume without  
5 affecting the printing process, providing the dopants  
6 have been micronised into fine powders of the order of  
7 1-4µm diameter. If this step is omitted poor  
8 uniformity printing results. Our dopants need add no  
9 colour to the ink, so give a colourless invisible  
10 printed strip onto the object to be protected.

11 Alternatively a colouring dopant can be selected to  
12 blend in with an existing coloured scheme.

13  
14 A major advantage of the dopants made in accordance  
15 with the present invention is that they are cheap and  
16 simple, not requiring the presence of complex expensive  
17 chemicals.

18  
19 The dopants can be applied to artefacts by any standard  
20 deposition technique - air spray, lacquering, printing,  
21 stamping.

22  
23 The dopants could also be directly incorporated into  
24 paper or plastic (for example) at time of manufacture  
25 of said paper or plastic. For our techniques to work  
26 it is not necessary that the dopants are added as a  
27 superior layer or film, although in many cases this  
28 will be the simplest and cheapest method. The fact  
29 that our dopant/excitation/detector technology does not  
30 require surface deposition can offer more  
31 security/covertness to the process. It arises because

1 the excitation methods we are employing have ranges of  
2 many tens of microns in common materials such as paper  
3 and plastics. Since dopants in accordance with the  
4 present invention need not be on the surface of the  
5 document the forger is denied the opportunity to scrape  
6 off samples from repeated small surface areas and  
7 analyse them to look for "surprising" changes in  
8 composition from area to area. Such changes give the  
9 forger a clue that covert technology is being used in  
10 that area.

11 The multiple peaks, troughs, and turning points  
12 resulting give rapid, positive, unambiguous  
13 identification of dopant presence (and hence object  
14 authenticity) and allow multiple dopants to be used as  
15 a further method of disguise, if required.

16  
17 The preparation of the inorganic powders for doping to  
18 permit identification by visible light is not limited  
19 to the use of chemical compounds which could be formed  
20 by precipitation from a solution because such compounds  
21 are limited in numbers. It has been found that the  
22 most useful compounds (those with the most distinctive  
23 absorption spectra in the visible) could be formed by  
24 fusion melting. Silicates, phosphates, borates have  
25 been found to be the most useful starting points for  
26 fusion, because they give transparent glass matrices.

27  
28 In forming the required solids for powdering, the  
29 chemical batch composition is not, for example, limited  
30 to that required to produce, say, a glass. This is  
31 because long range atomic order is not required in the

1 solid, since homogeneity is assured by micronising the  
2 composition. Indeed in general terms we have found  
3 that the best compositions are obtained where phase  
4 separation of the melt temperature is imminent. This  
5 point is determined experimentally for each  
6 composition. Nor need the chemistry be limited to  
7 stoichiometric ratios such as to arrive at crystalline  
8 compounds, e.g. as used to produce the commonplace  
9 inorganic fluorescence powders added to printing inks.

10

11 In many compositions, the structure and magnitude of  
12 the absorption peaks can be controlled over a wide  
13 range by control of the gas atmosphere during the melt  
14 phase. This is established by trial and error for each  
15 composition by test melting each composition in air, in  
16 a reducing atmosphere, and in an oxidising atmosphere  
17 to determine the optimum methodology and conditions for  
18 the absorption profile required.

19

20 In many compositions, the structure and magnitude of  
21 absorption peaks can be controlled by including a  
22 substantial quantity (>20% by weight) of a high atomic  
23 number Z element in the batch composition (lanthanum,  
24 bismuth, and strontium work well, as examples). Then  
25 varying the content of this high Z element only gives  
26 changes in position and magnitude of the absorption  
27 peaks, from composition to composition. Different  
28 absorption peak wavelengths and magnitudes from that  
29 exhibited by the raw dopant before being incorporated  
30 in a glass.

1 The effect of incorporating the dopant in a glass on  
2 its spectrum can be seen in Figs. 8, 9, 10 and 11.

3  
4 Fig. 8 shows a plot of the percent transmission against  
5 wavelength (nm) for a raw Europium Oxide dopant powder.

6 Fig.9 shows a plot of the percent transmission against  
7 wavelength (nm) for a Europium Oxide dopant powder  
8 incorporated in a glass and ground into a fine powder.

9 The substances contained in the glass are as given in  
10 Table 1 below and the glass plus dopant is made in  
11 accordance with the method given below Table 1 on page  
12 14.

13  
14 Simply from a visual inspection it can be seen that the  
15 two spectra are very different.

16 The feature of the spectrum of Europium Oxide shown at  
17 reference numeral 81 for the raw oxide powder that  
18 occurs at a wavelength of 533 nm has been shifted to  
19 531nm. A similar shift can be seen for the lower  
20 wavelength peaks 83 and 93. In both cases, the shift  
21 in wavelength was 2nm. The most significant difference  
22 between the spectra of Fig. 8 and Fig.9 is the presence  
23 of the line in the spectrum of the Europium Oxide  
24 contained in glass at 393nm. There is no similar line  
25 in the raw powder spectrum.

26  
27 Fig. 10 shows a plot of the percent transmission  
28 against wavelength (nm) for a raw Erbium Oxide dopant  
29 powder. Fig.11 shows a plot of the percent  
30 transmission against wavelength (nm) for an Erbium  
31 Oxide dopant powder incorporated in a ground fine

1 powder glass. As with the sample used to obtain the  
2 spectrum of Fig. 9, the substances contained in the  
3 glass are as given in Table 1 below and the glass plus  
4 dopant is made in accordance with the method given  
5 below Table 1 on page 14.

6  
7 Fig. 10 shows, at reference numeral 101, the existence  
8 of multiple peak structure occurring from a minimum  
9 point at 654nm to approximately 700nm. It can be seen  
10 that these features are absent from the spectrum of  
11 Fig. 11 as indicated at reference numeral 111.

12  
13 Fig. 10 also has multiple peak structure occurring from  
14 a minimum value at 521nm up to approximately 600nm.  
15 These features are absent from the spectrum of Fig. 11  
16 as can be seen at reference numeral 113.

17  
18 We have shown our dopant technology to work in a wide  
19 variety of compounds, including, but not limited to,  
20 silicates, borosilicates, borates and germanates.

21  
22 The following are a number of examples of the  
23 composition and method of manufacture of a doped glass  
24 in accordance with the present invention.

25

26 Example 1

27

28 A glass batch of a typical suitable composition is as  
29 follows.

30

1  
2

Compound	Wt %
SiO <sub>2</sub>	35%
B <sub>2</sub> O <sub>3</sub>	40.0
Na <sub>2</sub> O	8.5
K <sub>2</sub> O	8.5
Al <sub>2</sub> O <sub>3</sub>	1.0
MgO	4.0

3

4

Table 1

5

6 To this batch was added 0.1 to 25 wt% of Eu<sub>2</sub>O<sub>3</sub>. All  
7 powder sizes can be used but approximately 250 mesh is  
8 preferable. A wide range of crucibles can be used, a  
9 Platinum crucible was used in this case. The final  
10 batch is mixed and homogenised then it is added to the  
11 crucible heated to 845°C. The temperature is then  
12 increased at a rate of approximately 5 °C/min to 1200 °C  
13 the final melt temperature. It has been found that  
14 good quality melts are produced by holding the melt at  
15 the final temperature for between 2 and 2.5 hours  
16 before powdering the glass. For absorber products not  
17 visible to the naked eye, the natural emissions of Eu<sub>2</sub>O<sub>3</sub>  
18 may be quenched by the use of high concentrations of  
19 Eu<sub>2</sub>O<sub>3</sub> or by the inclusion of small < 1% quantities of  
20 nickel oxide, silver oxide or lead oxide as  
21 luminescence quenchers.

22

1 The following compositions may also be used

Compound	Wt (g)	Compound	Wt (g)	Compound	Wt (g)
SiO <sub>2</sub>	55	SiO <sub>2</sub>	70	SiO <sub>2</sub>	50
B <sub>2</sub> O <sub>3</sub>	65	B <sub>2</sub> O <sub>3</sub>	80	Be <sub>2</sub> CO <sub>3</sub>	20
Na <sub>2</sub> CO <sub>3</sub>	29	Na <sub>2</sub> CO <sub>3</sub>	29	SrCO <sub>3</sub>	20
K <sub>2</sub> CO <sub>3</sub>	20	K <sub>2</sub> CO <sub>3</sub>	20	Na <sub>2</sub> CO <sub>3</sub>	10
Li <sub>2</sub> CO <sub>3</sub>	5	Li <sub>2</sub> CO <sub>3</sub>	5	K <sub>2</sub> CO <sub>3</sub>	10
Al <sub>2</sub> O <sub>3</sub>	2	Al <sub>2</sub> O <sub>3</sub>	2	Li <sub>2</sub> CO <sub>3</sub>	5
MgO	8	MgO	5	Al <sub>2</sub> O <sub>3</sub>	2
				MgO	5

2  
3 Table 2  
4  
5

Compound	Wt (g)	Compound	Wt (g)
SiO <sub>2</sub>	35	SiO <sub>2</sub>	55
B <sub>2</sub> O <sub>3</sub>	80	B <sub>2</sub> O <sub>3</sub>	65
Be <sub>2</sub> CO <sub>3</sub>	40	Na <sub>2</sub> CO <sub>3</sub>	29
Na <sub>2</sub> CO <sub>3</sub>	29	K <sub>2</sub> CO <sub>3</sub>	20
K <sub>2</sub> CO <sub>3</sub>	20	Li <sub>2</sub> CO <sub>3</sub>	5
Li <sub>2</sub> CO <sub>3</sub>	5	Al <sub>2</sub> O <sub>3</sub>	2
Al <sub>2</sub> O <sub>3</sub>	2	MgO	8
MgO	8		

6  
7 Table 3  
8  
9  
10  
11  
12

1 Another suitable composition is of the type

2

3

Compound	Wt %
SiO <sub>2</sub>	51
B <sub>2</sub> O <sub>3</sub>	13
Al <sub>2</sub> O <sub>3</sub>	8
MgO	6
CaO	10
SrO	4
ZnO	4

4

5

Table 4

6

7 This is particularly suitable as a base for  
8 incorporating dopants for visible wavelength absorption  
9 detection because all the base elements have largely  
10 unfeatured absorption spectra.

11

12 Dopants have also been successfully incorporated into  
13 glass matrices with the following ranges of chemical  
14 composition.

15

16 30-56wt% SiO<sub>2</sub>,

17 5-35wt%, La<sub>2</sub>O<sub>3</sub>/Bi<sub>2</sub>O<sub>3</sub>/Sr<sub>2</sub>O<sub>3</sub>,

18 2-33wt% Li<sub>2</sub>O/K<sub>2</sub>O/Na<sub>2</sub>O,

19 0-6% Al<sub>2</sub>O<sub>3</sub>

20 wherein the La, Bi, Sr are examples of a suitable high

21 Atomic number component.

22



- 1 Incorporation of all three alkaline earth compounds,  
2 plus BaO, gives much reduced melting temperatures.  
3  
4 Preferred elements for dopant fabrication for visible  
5 wavelength absorption system  
6  
7 Barium Zinc  
8 Lanthanum Samarium  
9 Lead Praesodymium  
10 Magnesium Europium  
11 Strontium Boron-10  
12 Titanium Neodymium  
13 Chromium Holmium  
14 Iron Thulium  
15 Caesium Cadmium  
16 Molybdenum Antimony  
17 Nickel Erbium  
18 Tungsten Lutecium  
19 Cobalt Tin  
20 Sodium  
21 Potassium  
22 Terbium

Table 5

- 23  
24  
25 Improvements and modifications may be incorporated  
26 without deviating from the scope of the invention.